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DETONATION SYNTHESIS AND CRYSTAL STRUCTURE OF SIX-LAYER SILICON CARBIDE

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Results of an x-ray study of a single crystal of silicon carbide SiC 6H formed from silicon dioxide and graphite upon detonation are presented. The structure is determined by direct methods and is then refined using the full-matrix least-squares method in anisotropic approximation on the basis of 312 reflections to $R_1 = 0.0194$.

Data on an x-ray study of condensed explosion effluxes of mixtures of gibbsite $\text{Al}(\text{OH})_3$ (analytical grade) and hexogen $\text{C}_3\text{H}_6\text{N}_6\text{O}_6$ are presented in [1]. The special features of the experimental procedure for explosive mixtures are described in detail in [2]. It is found upon detonation of this mixture that along with $\alpha\text{-Al}_2\text{O}_3$ one more, unknown alumina modification ($\lambda\text{-Al}_2\text{O}_3$) is formed. In addition to gibbsite of analytical grade we performed a number of experiments on gibbsite containing the following additives (wt.%): 0.63 SiO_2 , 0.16 Na_2O , 0.17 MgO , 0.26 K_2O .

Microscopic study of condensed explosion effluxes of the mixture 20% $\text{Al}(\text{OH})_3$ – 80% $\text{C}_3\text{H}_6\text{N}_6\text{O}_6$ revealed several well-faceted crystals. Using the Laue method we managed to select a pale-green crystal applicable to the x-ray study, measuring $0.15 \times 0.15 \times 0.10$ mm.

Data on an x-ray microstudy of this crystal using the method described in [2] along with data on the unit-cell parameters and the Fedorov group symmetry indicated that the crystal is the modification SiC 6H.

An x-ray study of the SiC single crystal was performed at room temperature on a CAD-4 (Enraf-Nonius) diffractometer (Mo-K_α radiation, graphite monochromator, ω -2 θ scanning). The parameters of the hexagonal unit cell were refined using 25 centered reflections within the angle interval of $18 - 22^\circ$: $a = 3.081(1)$, $c = 15.122(5)$ Å, $V = 124.3$ Å³, $Z = 6$, Fedorov symmetry group $P6_3mc$.

Within the interval of $2 - 40^\circ$ we measured the intensities of 1273 reflections, 368 of which were independent. All the reflections forbidden by extinctions for the group $P6_3mc$ were lower in intensity than the threshold $3\sigma(I)$ except for two reflections with hkl (003) and (00 $\bar{3}$), which seems to be attributable to the effect of simultaneous reflections observed in [3]. Correction for absorption seemed unsuitable due to

the small size of the crystal and the small linear absorption coefficient.

The structure was determined by direct methods (SHELXS-86 [4]) and was then refined using the full-matrix least-squares method (SHELXL-93 [5]) in anisotropic approximation with 312 reflections and 19 refined parameters to $wR_2 = 0.0434$ and $R_1 = 0.0194$. Somewhat higher values of the divergence factors were obtained in calculation of the inverted structure, but the main criterion for the correctness of the absolute structure was a zero value of the parameter x of the absolute structure [5] for initial variant and $x = 1$ for the inverted variant. Atomic coordinates and equivalent isotropic thermal parameters are listed in Table 1. The interatomic spacing was as follows (Å): 1.899(3) for Si(1) – C(1), 1.891(3) for Si(2) – C(2), 1.892(3) for Si(3) – C(3), 1.887(1) for Si(1) – C(3)', 1.885(1) for Si(2) – C(1), and 1.886(1) for Si(3) – C(2).

A structural study of the crystal confirmed on the whole the results of most accurate study of the six-layer SiC polytype [3]. A certain limitation of the structural determination [3] is the lack of data on standard deviations of the atomic coordinates resulting from the poor convergence of the algorithm of the structure refinement within the framework of block-diagonal least-squares method (the full-matrix refinement was unstable). This was the reason for the author of [3] to perform a similar calculation using Fourier synthesis.

TABLE 1

Atom	<i>X</i>	<i>Y</i>	<i>Z</i>	$U_{\text{eqv}}, \text{\AA}^2$
Si(1)	0	0	0	0.0029(1)
Si(2)	2/3	1/3	0.16693(12)	0.0039(2)
Si(3)	1/3	2/3	0.33335(12)	0.0020(2)
C(1)	0	0	0.1256(2)	0.0036(4)
C(2)	2/3	1/3	0.2920(2)	0.0046(3)
C(3)	1/3	2/3	0.4585(2)	0.0029(3)

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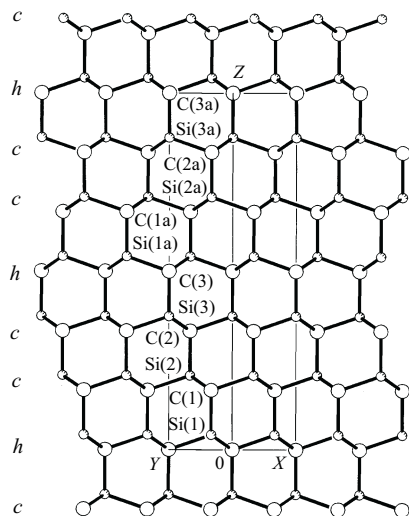


Fig. 1. Structure of the 6-layer SiC polytype, plane $(11\bar{2}0)$.

Thus, he obtained close, but not identical results. We also performed refinement of the structure but didn't face that problem, probably due to the use of a program [5] for all reflections having intensity higher than zero.

The structure of SiC 6H consists of almost the same SiC double layers alternating along the z axis in the sequence $ABCACB...$ (see Fig. 1). Another system of notation adopted for description of the most close-packed arrangements uses the character of the surrounding of the structural units of the given layer with the structural units of the two nearest layers, i.e., hexagonal h or cubic c surrounding. Layer interleaving in the SiC 6H structure occurs in the order $hcchcc...$.

Each of three independent Si atoms have an almost regular tetrahedral surrounding formed by four carbon atoms (and vice versa). A comparison of the interatomic spacings Si – C confirmed the conclusion made in [3] that the bonds directed along the z axis are longer than those directed obliquely. The spacing difference is more pronounced for the Si(1) atom (0.012 \AA) located in a layer having a hexagonal surrounding, whereas for the Si(2) and Si(3) atoms in layers having a cubic surrounding the spacing difference is much smaller (0.006 \AA). The average difference in the bond length 0.008 \AA obtained in the experiments matches the value $0.008(2) \text{ \AA}$ determined from data on the lattice vibrational frequency, compressibility, and temperature coefficient of linear expansion for SiC 6H [3, 6]. The values of the angles

at the Si atoms are close to ideal tetrahedral angles and lie within the narrow interval of $109.36 - 109.59(9)^\circ$.

Calculation of the Si – C spacing for the two-layer modification SiC 2H using data of [7] gives 1.893 \AA for the bonds directed along the c axis and 1.885 \AA for the bonds directed obliquely. Regular tetrahedral coordination (the Si – C spacing is 1.887 \AA) is observed in the cubic modification of SiC [8].

It is known that rapid formation of silicon carbide occurs upon annealing a batch containing carbon and silicon dioxide. The onset of crystallization of SiC is observed at a temperature of $1400 - 1500^\circ\text{C}$. Complete crystallization is attained at 1700°C . For a mixture of 20% gibbsite and 80% hexogen the theoretical temperature of the explosion is about 2000°C .

Hexogen $\text{C}_3\text{H}_6\text{N}_6\text{O}_6$ decomposes into CO_2 , CO , H_2O , H_2 , and N_2 under explosion. The negative oxygen balance governs the presence of free carbon in the condensed effluxes of the explosion. A very thin and most intense graphite line is seen on the x-ray pattern of these products.

The pale-green color of the crystal can be attributed to small quantities of nitrogen [9] incorporated into the SiC lattice upon explosion of the hexogen. Note that in the same experiment we found a single crystal that is close in composition to SiO_2 . This compound crystallizes in the triclinic system.

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